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Stereoelectronic effects in the reactivity of electrogenerated cation radicals of arylselenides

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Abstract

The role of stereoelectronic effects in the electrochemical oxidation of arylselenides Se-substituted by a trimethylsilylmethyl group and those with substituents bearing a carbonyl group have been considered. Although the HOMO of these compounds is formed of p_z-type electrons of the ArSe moiety, the predominant contribution from the lone pair of Se makes the heteroatom more susceptible to direct electronic effects than to effects transmitted through the aromatic ring. The σ-p hyperconjugation and the interaction through space were shown to lower the charge localization on the reaction center and to stabilize cation radicals of these compounds, thus changing the control of the potential-determining reaction and promoting second order reactions.

Keywords: Electrooxidation; Cation radicals; Arylselenides; Silicon organic compounds; Reactivity; Stereoelectronic effects

1. Introduction

Electrochemical oxidation of a large number of organic selenides has been studied to date [1–7]. When the reversibility of electron transfer was proved electrochemically, electrogenerated cation radicals were shown to react in first (rupture either of $Se–C_{sp3}$ or $C_{sp3}–H$ bond [8–11]) or second (disproportionation, dimerization [1,12–14]) kinetic order ensuing bulk reactions. A necessary and sufficient condition for the second order reactions to occur is the presence in the molecule of diorganylselenide of two aromatic groups which are immediately bound to the selenium atom [5,12,13,15]. If only one or no aromatic fragment is linked to selenium, first order reactions of cation radicals (if not dissociative electron transfer at all) take place [8–10,16]. The feature which accounts for this discrimination is a specific combination of two factors: the electronic structure of the frontier orbitals of these compounds and the energy of the weakest bond adjacent to selenium. The ability of arylselenides to give electrons in oxidation reactions is determined by the nature of their HOMO formed with the lone pair of selenium and π-electrons of one aromatic ring [17–19]. In other words, the ArSe moiety is the fragment which is mainly responsible for the primary redox properties of arylselenides in oxidation processes. Obviously, it is not the electronic structure of the second aryl which determines the occurrence of second order reactions of diarylselenides because there is not any significant conjugation between the orbitals of selenium and the π-system of the second aromatic ring [20]. The reason why the second order potential-determining reactions are inherent to diarylselenides is higher dissociation energy of the $Se–C_{sp2}$ bond compared to the $Se–C_{sp3}$ bond strength [21] and the fact that the deprotonation of an aromatic ring is very unfavorable.

The possibility for cation radicals of arylselenides other than Ar_2Se to react in second order reactions was only shown for arylethynylselenides ArSeC≡CAr [14] having no acid α-protons, and for arylmethylselenides ArSeMe, whose methyl group is not stable enough as a leaving group [22] to enable direct cleavage of the cation radical. In the last case, the rupture of the $Se–C_{sp3}$ bond in the cation radicals is very unfavorable, and the only possible potential-determining reaction is

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